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VARIABILITY OF HEAVY METAL CONCENTRATIONS IN WATERS OF FISHPONDS AFFECTED BY THE FORMER LEAD AND ZINC MINE IN SOUTHERN POLAND

The fluctuations of heavy metal (Cd, Pb, Zn, Mn and Fe) concentrations and physicochemical parameters of water were studied for five fishponds located in the Matylda catchment affected by the former Pb and Zn ore mine in the Upper Silesian Industrial Region, southern Poland. Generally, metal concentrations in dissolved phase in pond water were low for most of the year, but their drastic increases were periodically observed (up to Cd 5.8, Pb 147.3, Zn 800.3, Mn 987.8, and Fe 2532.8 $\mu g \cdot dm^{-3}$). The factors determining metal concentrations in the pond water have been discussed.

1. INTRODUCTION

Metal mining and processing cause usually severe contamination of nearby lands. Metal contamination of soils and sediments in such areas is an important problem even many years after cessation of the ore processing [1–3]. Heavy metal concentrations in contaminated sediments [1–4] exceeding several times the values of toxic effect threshold (TET) (Cd 3, Pb 170, and Zn 540 $\mu g \cdot g^{-1}$ according to EC and MENVIQ [5]) above which sediments are considered heavily polluted and having detrimental effects on sediment-fed organisms. For cleaning metal-polluted sediments and soils *in situ* or *ex situ* phytoremediation is frequently used [6].

Metals can be remobilized from contaminated sediments under favorable environmental conditions (pH, redox potential, frequent resuspension) [7, 8]. Mobilization of heavy metals from sediments due to complex biological, physicochemical, and hydro-

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logical processes [1, 9] is conducive to appearance of high concentrations of heavy metals in water and might cause a serious environmental threat. Therefore it is necessary to investigate the fate of trace metals in hydrosystems impacted by mining wastes.

Olkusz and Chrzanów lead-zinc mining areas in the Upper Silesian Industrial Region in Southern Poland provide a unique example of the industrial impact on the aquatic environment. The history of zinc-lead mining activities which began in this area in 13th century lasts up today, whereas the Matylda Stream itself situated in this area received mine waters from the Pb-Zn mine Matylda in Chrzanów in 19th and 20th centuries. Even though the mine has been closed for over 40 years, sediments of the Matylda Stream and fishponds built already in 19th century in order to utilize mine water, situated in the middle course of the stream, are still heavily contaminated with Pb, Zn and Cd [4]. Despite this, the structure of biotic elements (algae, zooplankton) in the fishponds during the vegetation season is fairly rich in species [10]. However, genom alteration of some Chironomidae species living in the sediment of the Matylda Stream was related to high metal contamination [11]. The decline of the macrophyte species (*Myriophyllum spicatum*) in one of the fishponds [4] after periodical increase in the concentrations of heavy metals in the pond water also indicated detrimental effect of contaminants there.

The aim of the present paper was to study the variability of the dissolved phase of trace metals and macroions in water of fishponds situated in the middle part of the Matylda catchment affected by effluents from the former lead and zinc mine.

2. MATERIALS AND METHODS

Study area and sampling. The Matylda catchment (Fig. 1) is situated in the Upper Silesian Industrial Region in southern Poland. It was affected by the former lead and zinc ore mine in Chrzanów which operated from 1850 to 1973. During this time the Matylda stream received variable amounts of mine water which exceed natural river discharge by even 100 times [4]. In the time of mine operation groundwater seepage combined with surface drainage caused pollution of sandy soils exceeding over 100 $\mu g \cdot g^{-1}$ of Cd, 24% of Zn and 4% of Pb at surface or subsurface soil horizons, and reaching at least 60 cm in depth [12]. Since 1973 the Matylda stream with the discharge of about 10 $dm^3 \ s^{-1}$ in its middle reach has drained a small catchment of a dozen or so square kilometers.

Five fishponds were investigated in the Matylda catchment (Fig. 1). The Upper Pond (UP) was located in the upper part of the catchment, closest to the former metal mine. A cascade of three ponds in the middle part of the catchment consists of an upper Small Pond (SP), a middle Medium Pond (MP) and the largest Lower Pond (LP). The first of the cascade of ponds (SP) was directly supplied with water from the Matylda Stream. One more, lower pond (LoP) was situated in the lower part of the catchment

and supplied both with the waters from the cascade of ponds and relatively unpolluted tributary. The depth of the ponds reaches 2 m. During the pond operation, a part of sediments was removed from the UP and LoP ponds, whereas in the LP sediments were shifted with a bulldozer toward the southeast banks of the pond. Sediments of the MP and SP ponds were intact.
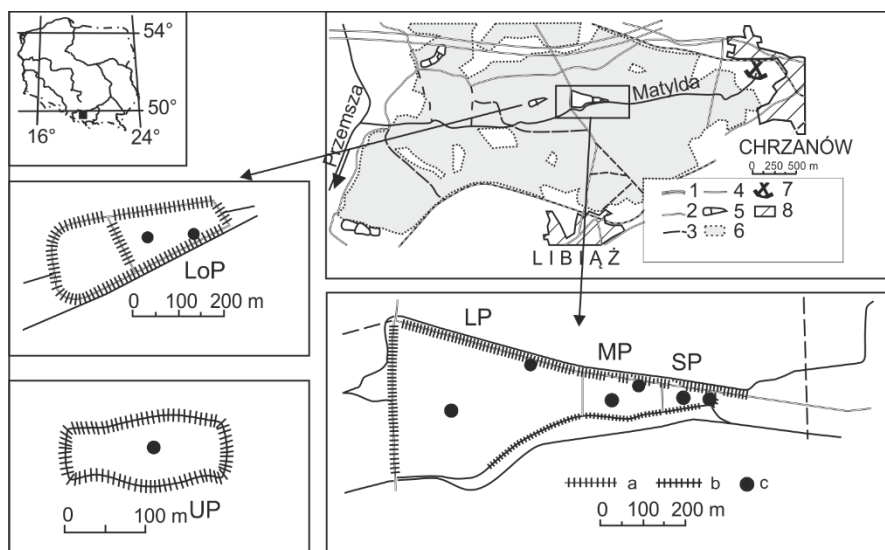

Fig. 1. Locations of the research area and sampling points: a) dykes and roads, b) dykes, c) sampling points. UP – upper pond, SP – small pond, MP – middle pond, LP – large pond, LoP – lower pond; 1 – highway, 2 – main roads, 3 – forest roads, 4 – railways, 5 – fish ponds, 6 – forests, 7 – closed Matylda mine, 8 – built-up area

Samples of water (surface layer) were collected from the central and near-bank parts of the SP, MP, LP and LoP ponds and from the UP only of its central part. The samples were taken monthly from April 2009 to March 2010 except of July 2009 (all ponds) and September 2009 (central parts of SP, MP, LP and LoP). The sampling on dry spring of 2009 (April and May) was followed by wet early summer with rainfalls in June exceeding a multi-year average by 150%. The following August, September and October were warmer and dryer than average (rainfalls of 50–75% of norm). Soon after the sampling in October rains and snowfall of about 60 mm raised water level both in ponds and in their tributaries. Sampling in November represented wet period with low temperatures reducing evaporation. Winter started at the end of December and sampling in January was preceded by monthly period of frosts and accretion of ice cover to the thickness of 10–15 cm. Sampling was finished at the end of March after rapid snow melting, preceded by over one month of temperatures fluctuated about 0 °C. A permanent ice cover lasted until the end of March. In the collected samples, the following

parameters were determined: pH, conductivity, dissolved oxygen, anions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+), BOD_5, organic matter (LOI) and concentrations of heavy metals (Cd, Pb, Zn, Mn and Fe).

Physicochemical analysis. Conductivity and pH were determined using WTW (Multi 340 and SET 2) apparatus, whereas dissolved oxygen and BOD_5 by the Winkler method. In order to analyze the content of anions and cations (heavy metals as well) water samples were filtered through 0.45 μm pore-sized syringe filters into a polyethylene container. The contents of inorganic ions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+) were determined within 48 h using ion chromatography (DIONEX ICS 1000 and IC DX 320). For the metal analysis, samples of water were acidified to pH < 2 with ultrapure HNO_3. The concentrations of Zn, Cd, Pb, Fe and Mn were measured with an inductively coupled plasma mass spectrometer (Perkin Elmer ELAN 6100). The organic matter was determined as losses on ignition (LOI) at 550 °C.

The differences in the heavy metal concentrations in water between the studied ponds were analyzed using the Kruskal–Wallis test, while those within one pond between its central and coastal parts by the Wilcoxon test. The relationships between the concentrations of heavy metals and the values of physicochemical parameters were determined by the Spearman correlation.

3. RESULTS

3.1. PHYSICOCHEMICAL PARAMETERS OF WATER

The values of physicochemical parameters in the studied ponds (median, range) are given in Table 1. The water of SP, MP, LP and LoP had pH of 7.0–9.7, while pH in UP varied in the range of 4.9–7.6. During the most of the year, the water of UP had acidic reaction. pH was significantly lower in UP than in MP and LP (Table 2). In all ponds, pH was usually higher in spring and summer and then decreased reaching the lowest values in winter months (January–March) (Fig. 2).

The waters of SP, MP, LP and LoP were usually well oxygenated (>8 mg $O_2 \cdot dm^{-3}$), while that of UP weakly oxygenated (<4 mg $O_2 \cdot dm^{-3}$). However, a decrease in the amount of dissolved oxygen below 4 mg $O_2 \cdot dm^{-3}$ appeared also periodically in the waters of SP and LP in the summer, autumn and winter months (Fig. 2). The content of dissolved oxygen was significantly lower in the water of UP than that of other ponds (Table 2).

The amounts of anions and cations varied among the studied ponds (Table 1). The median values of conductivity, Cl^-, SO_4^{2-}, HCO_3^-, Ca^{2+} and Na^+ were the highest in the water of SP (the first of the cascade of ponds directly supplied with waters from the Matylda stream), while that of Mg^{2+} occurred in LP (the last of the cascade). The lowest

median contents of major anions and cations (with the exception of K^+) were found in the water of UP (Table 1). Low values of studied anions and cations were also found in LoP (supplied both with waters from the cascade of ponds and from the relatively un-polluted tributary). Occasionally drastic increase in the contents of major anions and cations appeared in the pond waters (UP in May and September; in the central and near-bank parts of SP in April and May, Fig. 3), which were not accompanied by high con-centrations of heavy metals.

The values of BOD_5 (the content of easily degradable organic matter) varied in the range 0.3–8.2 mg $O_2 \cdot dm^{-3}$ and the amount of LOI in the range 15–262 mg·dm^{-3} (Table 1). The values of BOD_5 and contents of LOI were similar in the studied ponds and increased in different months. Moreover, the amount of nitrates was lower during growing season and higher in autumn and winter months.

Table 1

Median (M) and range (R) values of physicochemical parameters and concentrations
of heavy metals in waters of the ponds situated in the Matylda catchment

Parameter	UP		SP		MP		LP		LoP	
	M	R	M	R	M	R	M	R	M	R
pH	6.3	4.9–7.6	7.5	7.0–8.5	7.9	7.0–8.9	8.3	7.0–9.7	7.4	7.0–8.6
Conductivity, $\mu S \cdot cm^{-1}$	215.5	110.0 –1125.0	481.0	259.0 –636.0	432.0	245.0 –490.0	434.0	140.0 –488.0	373.0	257.0–429.0
Dissolved O_2, mg·dm^{-3}	3.8	0.5–5.4	8.6	1.6–12.0	9.3	5.8–10.6	9.5	1.9–11.7	9.1	4.6–11.5
Cl^-, mg·dm^{-3}	19.0	13.0–43.8	27.2	13.5–37.4	23.5	16.7–32.9	24.5	9.6–31.4	20.8	11.8–25.8
HCO_3^-, mg·dm^{-3}	48.1	9.3–445.2	151.9	59.1–261.2	134.2	69.4–202.1	129.8	41.8–162.3	125.2	63.6–192.1
SO_4^{2-}, mg·dm^{-3}	47.5	27.9–230.1	80.2	46.1–136.6	77.5	38.8–111.4	75.3	20.7–98.7	48.6	25.6–75.3
Na^+, mg·dm^{-3}	8.5	2.8–29.0	13.8	9.0–19.7	12.3	6.9–17.0	12.5	4.2–16.1	10.8	6.9–13.2
K^+, mg·dm^{-3}	2.7	1.7–10.8	3.2	2.0–6.3	3.0	1.1–3.9	2.8	0.8–4.5	2.4	1.7–3.2
Ca^{2+}, mg·dm^{-3}	23.2	12.1–152.3	60.2	30.5–86.8	52.3	27.4–66.4	52.0	16.3–64.5	45.1	31.5–54.2
Mg^{2+}, mg·dm^{-3}	5.0	2.2–42.8	13.5	6.4–23.9	11.9	4.9–16.0	13.8	3.0–15.0	10.6	6.4–12.3
NO_3^-, mg·dm^{-3}	0.63	0.05–2.85	2.15	0.03–18.62	1.99	0.02–10.10	0.76	0.02–18.32	0.65	0.02–22.28
NH_4^+, mg·dm^{-3}	0.22	0.03–4.61	0.09	0.02–0.90	0.08	0.02–0.38	0.08	0.01–0.49	0.13	0.03–0.21
BOD_5, mg·dm^{-3}	2.0	0.3–3.4	2.9	0.3–6.4	3.2	1.0–8.2	1.9	0.3–5.8	2.1	0.5–5.3
LOI, mg·dm^{-3}	111.0	68.0–155.0	121.0	52.0–195.0	117.0	61.0–262.0	124.0	15.0–191.0	111.0	68.0–155.0
Cd, $\mu g \cdot dm^{-3}$	2.9	0.03–5.80	0.9	0.02–4.48	0.2	0.02–2.60	0.06	0.02–1.16	0.3	0.02–1.91
Pb, $\mu g \cdot dm^{-3}$	8.4	1.3–75.7	10.8	2.4–147.3	4.6	1.6–18.0	5.5	1.1–106.0	5.6	1.6–10.7
Zn, $\mu g \cdot dm^{-3}$	483.6	64.6–800.3	344.4	13.7–790.8	61.1	10.4–561.5	25.8	2.6–291.3	68.8	7.1–289.4
Mn, $\mu g \cdot dm^{-3}$	120.4	94.7–287.8	85.3	13.4–987.1	26.9	4.8–190.6	19.7	3.7–87.8	106.8	10.7–293.5
Fe, $\mu g \cdot dm^{-3}$	805.9	164.4–2532.8	171.5	2.0–1124.6	96.1	49.8–297.5	59.8	1.3–1100.1	251.3	67.0–639.0

UP – upper pond, cascade of ponds: SP – small pond, MP – middle pond, LP – large pond, LoP – lower pond, LOI – loss of ignition.

The significance of differences in the values of physicochemical
parameters and heavy metal concentrations in the waters
of the studied ponds in the Matylda catchment[a]

Parameter	The value of statistics	Ponds
Dissolved O_2	$H_{5,103} = 25.98$, $p = 0.0001$	UP < SP, MP, LP, LoP
pH	$H_{9,104} = 24.55$, $p = 0.0002$	UP < MP, LP
Conductivity	$H_{9,104} = 34.41$, $p = 0.0000$	SP > LoP, UP
Cl^-	$H_{5,104} = 15.58$, $p = 0.0082$	SP > LoP
SO_4^{2-}	$H_{5,104} = 31.74$, $p = 0.0000$	SP, MP, LP > LoP
Na^+	$H_{5,104} = 22.67$, $p = 0.0004$	SP > UP, LoP
K^+	$H_{5,104} = 24.83$, $p = 0.0002$	SP, MP > LoP
Ca^{2+}	$H_{5,104} = 34.16$, $p = 0.0000$	SP > UP, LoP
Mg^{2+}	$H_{5,104} = 31.06$, $p = 0.0000$	SP, LP > LoP
Cd	$H_{5,103} = 16.20$, $p = 0.0063$	UP > LP
Pb	$H_{5,103} = 27.19$, $p = 0.0001$	SP > LP, LoP
Zn	$H_{5,103} = 17.38$, $p = 0.0038$	UP > LP
Mn	$H_{5,103} = 50.37$, $p = 0.0000$	LoP > MP, LP SP, UP > LP UP > MP
Fe	$H_{5,103} = 49.97$, $p = 0.0000$	UP > MP, LP SP > LP LoP > MP, LP

[a] The Kruskal–Wallis test, the value of p for multiple comparisons. Only
significant differences are given. UP – upper pond, cascade of ponds:
SP – small pond, MP – middle pond, LP – large pond, LoP – lower pond,
p – significance level.

The concentration ranges of heavy metals in the pond waters ($\mu g \cdot dm^{-3}$) were:
Cd 0.02–5.80, Pb 1.1–147.3, Zn 2.6–800.3, Mn 3.7–987.0 and Fe 1.3–2533 (Table 1,
Figs. 2 and 4). There were marked differences among the studied ponds in them.
Higher median concentrations of Cd, Pb, Zn and Fe were found in the waters of UP
and SP located closer to the discharge point of mine waters than in the remaining
ponds (Table 1). The differences of median concentrations of the investigated metals
between UP and the remaining ponds were considerable for: Cd (2–48 times), Fe
(3–13 times), Pb (1.5–4 times) and Zn (4–18 times). A decrease in the median heavy
metal concentrations down the cascade of ponds – SP, MP and LP – was larger in the
central part of ponds than at their banks. Differences in median values between SP
and LP for Zn equal 11 times, for Cd – 7 times, while for Pb, Mn and Fe 2.2–3.2 times.
Differences in concentrations of Pb, Mn and Fe between SP and LP, as well as of Pb
between SP and LoP were statistically significant (Table 2). The concentrations of Mn
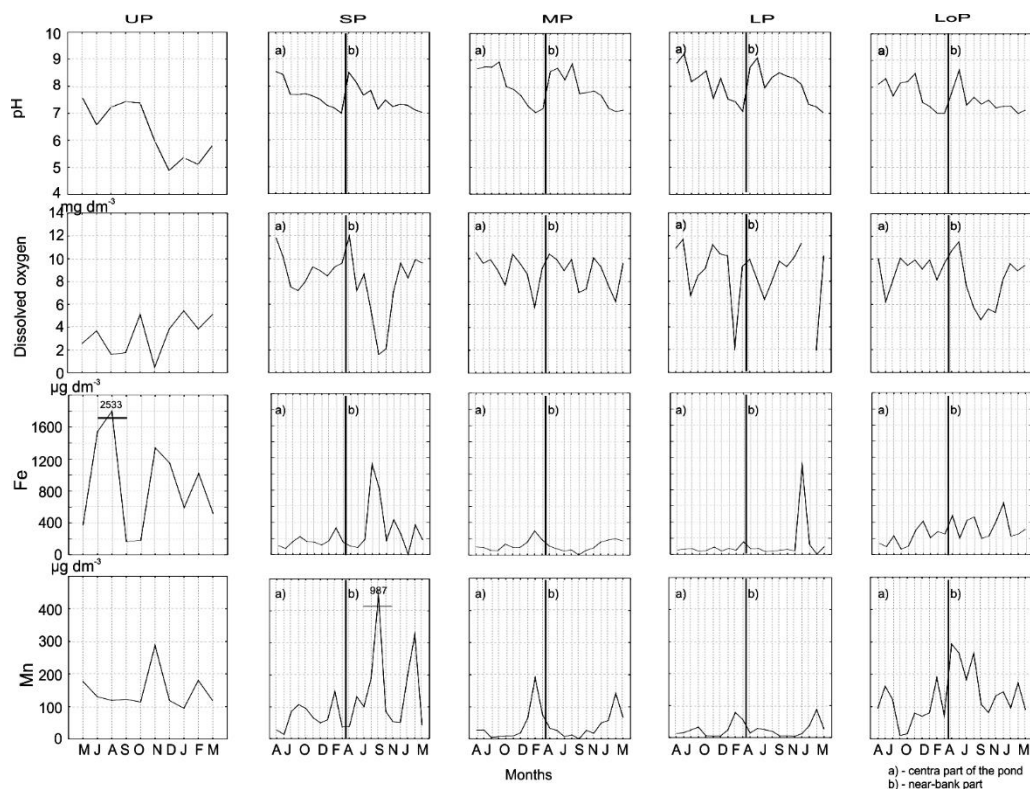and Fe in the waters of MP and LP were significantly lower than of UP and LoP
(Table 2).

Fig. 2. Dissolved oxygen content, pH, and the concentrations of Mn and Fe
in the surface water of the studied ponds in the Matylda catchment

The concentrations of heavy metals and values of some parameters also showed marked differences among the studied parts of the ponds. Significantly higher concentrations of Mn ($Z = 1.99$, $p = 0.047$) Cu ($Z = 2.37$, $p = 0.018$) and Na^+ ($Z = 1.99$, $p = 0.047$) in SP, Mn ($Z = 2.60$, $p = 0.009$), Fe ($Z = 2.60$, $p = 0.009$), Zn ($Z = 2.29$, $p = 0.022$) and NO_3^- ($Z = 1.99$, $p = 0.047$) in LoP, while lower pH ($Z = 2.55$, $p = 0.011$) and SO_4^{2-} content ($Z = 2.60$, $p = 0.009$) in MP were found in the coastal in comparison to the central parts of the ponds.

3.2. HEAVY METALS IN WATER

During most of the year concentrations of heavy metals in pond waters were relatively low but periodically their considerable increases were found (Figs. 2 and 4). High concentrations of heavy metals in UP occurred in various months, while in the cascade of ponds and LoP mainly in winter months until March and additionally in SP in late

summer and LoP in spring and summer. In winter months they usually occurred in central and/or near-bank parts, while in late summer and early autumn only in the near-bank parts. In general, high concentrations of heavy metals in the water of cascade ponds and LoP were found at neutral reaction (Figs. 2 and 4). As was mentioned above, water in UP had slightly acidic or neutral reaction during most of the year.
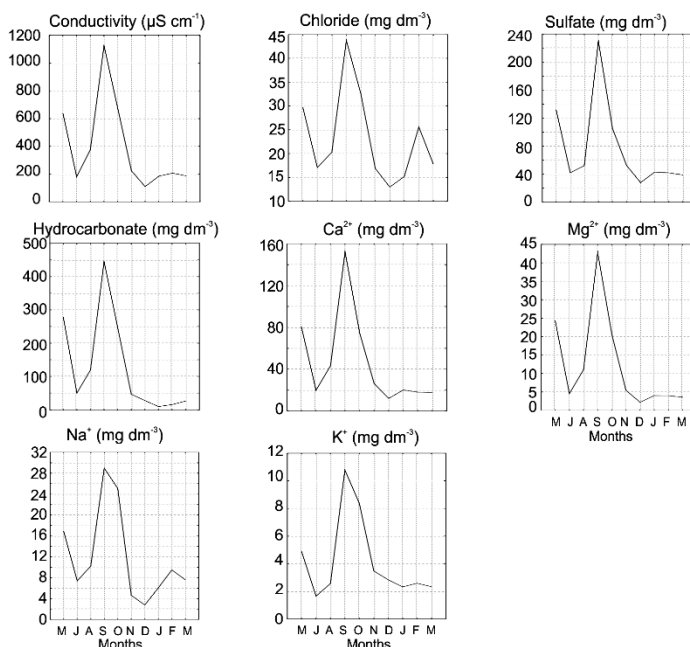

Fig. 3. Conductivities and the content of major ions in the surface water
of the Upper Pond in the Matylda catchment

High concentrations of heavy metals were found at low content of dissolved oxygen (<2 mg $O_2 \cdot dm^{-3}$) and increased content of NH_4^+ (0.38–0.90 mg·dm^{-3}). In such conditions, maximum or high concentrations of Pb and Fe appeared in August, of Mn, Fe, Cd, and Zn in November in UP, those of Mn and Fe in SP in September, whereas those of Mn and Pb in February in LP (Figs. 2 and 4).

High concentrations of heavy metals in the pond waters were also related to the high content of organic matter (expressed as BOD_5 4.3–8.2 mg $O_2 \cdot dm^{-3}$ and LOI 145–262 mg·dm^{-3}), and occasionally to NH_4^+ (0.4–0.9 mg·dm^{-3}) and some other ions (Cl^- 30.4–32 9 mg·dm^{-3}, Na^+ 15–17 mg·dm^{-3}). In the water of UP, maximum concentrations of Cd, Zn and the values of BOD_5 were found in January, high contents of Cd, Zn and the values of BOD_5 in June. In the near-bank part of SP, the high concentrations of Cd and Pb and LOI were found in January; Cd, Zn, Mn and the values of BOD_5 in February; Cd, Zn, and LOI in well oxygenated water (>8 mg $O_2 \cdot dm^{-3}$) in March, while

those of Cd, Pb, Zn, Fe and the value of BOD_5 in August. In both parts of MP, high concentrations of Cd, Pb and Zn, LOI, Cl^- and Na^+ ions and the values BOD_5 (only central part) were found in January, while of Cd, Pb, Zn, Mn, Fe, $N-NH_4$, Cl^- and Na^+ ions in February. In the coastal part of LP, the maximum concentration of Fe and elevated values of BOD_5 were found in December. In LoP high contents of Cd, Zn and LOI occurred in both parts of the pond and of NH_4^+ in its central part from January to March, while Fe, LOI, SO_4^{2-} in both parts and Pb in the central one in December. Additionally, maximum content of Pb, high values of LOI and of all studied ions accompanied by a minimum content of dissolved oxygen (4.6 mg $O_2 \cdot dm^{-3}$) were found in LoP in September.
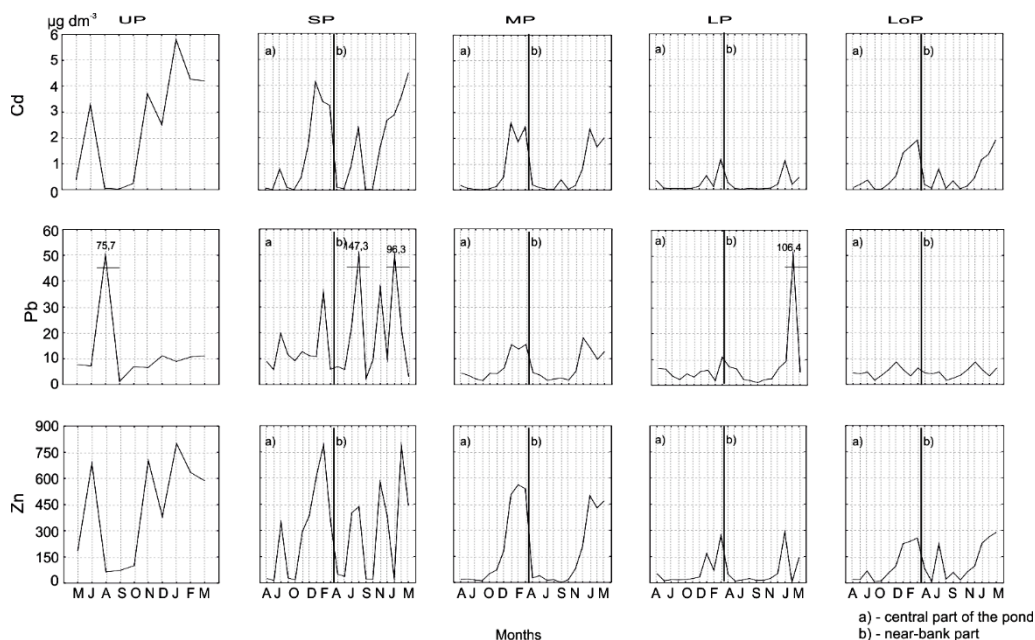

Fig. 4. The concentrations of Cd, Pb, and Zn in the surface water
of the studied ponds in the Matylda catchment

Moreover, a lack of relationship between high metal concentrations and the values of studied parameters was found. High concentrations of Cd, Zn and Fe accompanied by minimum concentrations of major anions and cations (SO_4^{2-}, HCO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}) and low contents of organic matter (BOD_5, LOI) were found in the central part of LP in March. High concentrations of Mn in LoP did not also show any clear relationships with other parameters.

During the whole studied period, metal concentrations in pond water depended (negative correlations) on pH (Cd in UP; Cd, Zn and Fe in SP; Cd, Pb, Zn, Mn and Fe in MP; Cd, Zn and Mn in LP; Cd and Zn in LoP) and on the amount of dissolved oxygen (Mn in UP and SP; Mn and Fe in LP) (Table 3).

Table 3

The relationship between concentrations of heavy metals and values
of physicochemical parameters in water of the studied ponds in the Matylda catchment

Parameter	Pond						Pond				
	UP	SP	MP	LP	LoP		UP	SP	MP	LP	LoP
	N						N				
	10	21	21	21	21		10	21	21	21	21
	Cd						Fe				
pH	–0.72	–0.62	–0.81	–0.46	–0.76		ns	–0.44	–0.78	ns	ns
Dissolved O_2	–						–0.44	–0.78	ns	ns	ns
Conductivity	–0.65	–0.68	ns	ns	–0.69						
SO_4^{2-}	ns	–0.45	ns	–0.44	ns		ns	–0.46	ns	ns	ns
HCO_3^-	–0.92	–0.75	–0.54	ns	–0.65		ns	ns	–0.56	ns	ns
Na^+	–0.64	–0.47	ns	ns	–0.49		ns	ns	ns	ns	–0.51
K^+	ns	–0.84	ns	ns	–0.57						
Ca^{2+}	–0.66	–0.58	ns	ns	–0.66		ns	ns	ns	ns	–0.46
Mg^{2+}	–0.71	–0.78	–0.48	–0.51	–0.66		ns	ns	–0.56	ns	ns
NO_3^-	ns	0.59	0.65	0.63	0.68		ns	ns	0.60	ns	0.51
NH_4^+	ns	ns	0.75	ns	ns		ns	ns	0.56	ns	ns
BOD_5	ns	ns	–0.56	ns	–0.56						
LOI	ns	0.48	0.48	ns	ns		0.65	ns	ns	ns	ns
	Pb						Mn				
pH	ns	ns	–0.79	ns	ns		ns	ns	–0.76	–0.46	ns
Dissolved O_2	–						–0.74	–0.60	ns	–0.60	ns
SO_4^{2-}	–0.66	ns	ns	ns	ns						
HCO_3^-	ns	ns	–0.55	ns	ns		ns	ns	–0.49	ns	ns
Mg^{2+}	ns	ns	–0.48	ns	ns		ns	ns	–0.55	ns	ns
NO_3^-	ns	0.45	0.69	ns	ns		ns	ns	0.61	ns	ns
NH_4^+	ns	ns	0.60	ns	ns		ns	ns	0.69	0.67	0.54
BOD_5	ns	ns	–0.55	ns	ns		–				
	Zn					Interactions between metals					
pH	ns	–0.49	–0.86	–0.51	–0.86	Cd–Pb	ns	ns	0.94	0.70	ns
Conductivity	–0.64	ns	ns	ns	–0.71	Cd–Zn	0.89	0.80	0.92	0.75	0.94
Cl^-	–0.66	ns	ns	ns	ns	Pb–Zn	ns	0.44	0.92	ns	ns
SO_4^{2-}	ns	ns	ns	–0.45	ns	Mn–Fe	ns	0.46	0.85	ns	ns
HCO_3^-	–0.73	–0.49	–0.60	ns	–0.75	Mn–Cd	ns	ns	0.83	ns	ns
Na^+	–0.72	ns	ns	ns	–0.50	Mn–Pb	ns	0.44	0.78	ns	ns
K^+	ns	–0.59	ns	ns	–0.59	Mn–Zn	ns	ns	0.80	ns	ns
Ca^{2+}	ns	ns	ns	ns	–0.66	Fe–Cd	ns	ns	0.86	0.50	ns
Mg^{2+}	ns	–0.59	–0.52	–0.45	–0.65	Fe–Pb	ns	ns	0.87	0.45	ns
NO_3^-	ns	0.55	0.79	0.59	0.74	Fe–Zn	ns	0.55	0.89	0.51	0.49
NH_4^+	–0.66	ns	0.65	ns	ns	–					
BOD_5	ns	ns	–0.55	ns	–0.52	–					

UP – upper pond, cascade of ponds: SP – small pond, MP – middle pond, LP – large pond, LoP – lower pond, LOI – loss of ignition.

The positive correlations were found between the metal concentrations and the content of nitrates (Cd, Pb, and Zn in UP; Mn, Fe, Cd, Pb and Zn in MP; Cd and Zn in LP; Cd, Zn, and Fe in LoP), values of NH_4^+ (Mn, Fe, Cd, Pb and Zn in MP; Mn in LP and LoP). There were also positive correlations between the pairs of metals (Cd–Zn in UP; Fe–Mn, Cd–Zn, Pb–Zn, Mn–Pb, Fe–Zn in SP). In general, the heavy metal concentrations in the studied ponds showed negative correlations with the content of anions, i.e. Cd, Pb, Zn, Mn and Fe with SO_4^{2-} and HCO_3^-; Zn with Cl^- (Table 3).

4. DISCUSSION

The characteristic feature of the chemical composition of water of the studied ponds were the increased amounts of sulfates and hydrocarbonates in comparison to the natural waters of southern Poland [13]. It was associated with predominance of carbonates, bearing sulfidic Zn-Pb ores, which outcrop in the Matylda catchment [14]. Besides natural sources which affect chemical composition of the studied waters during a year, also pond and stream sediments, as well as contaminated soils of the catchment and occasional, uncontrolled discharge of domestic effluents in the upper part of the catchment [2] can periodically increase the contents of anions and cations in pond water. It was found [12] that after the mine closure in the 1970s densely forested floodplain of the Matylda Stream, dissected by the network of ditches became a source of irregular increase of major ions (Ca, Mg, chlorides, carbonates and nitrates) in groundwater. The increased contents of major ions and metals in SP filled with mine-originated deposits of the thickness even up to 1 m suggests that the sediments were their considerable source.

The seasonal changes of decomposition of organic matter undoubtedly affect water oxygenation. The studied ponds (with the exception of UP) were well oxygenated during the most of the year whereas weakly (<2 mg $O_2 \cdot dm^{-3}$) only periodically. Hence, deduced changes in the sediment redox conditions may affect the concentrations of the most sensitive elements (like Mn in SP, LP, LoP and LP; Fe in SP) in the water of studied ponds that is typical of varied aquatic ecosystems [15–18]. Maximum or high concentrations of metals in the pond waters under reducing conditions accompanied by dissolved oxygen content in the range of 0.5–1.9 mg $O_2 \cdot dm^{-3}$ and slightly acidic and neutral conditions indicate their possible release from the bottom sediments. This has been expected because the pond sediments are still heavily contaminated with Cd (130–340 $\mu g \cdot g^{-1}$), Zn (10 000–50 000 $\mu g \cdot g^{-1}$) and Pb (4000–12 000 $\mu g \cdot g^{-1}$), and the amounts of these metals in reducible phase are large and varied in the range 50–80% on average [2]. It is well known that under reduced conditions, metals bound to easily reducible fraction may be released after decomposition of Fe and Mn oxides [19]. Such "internal loading" the best observed in SP largely filled with organic deposits, seems to

be a considerable source of the metals in the waters of the Matylda ponds. This phenomenon was also observed in other water bodies [20, 13]. Although the water contamination caused by this process occurred occasionally, mostly in winter (February) but also in summer (August and September) and autumn (November), its magnitude evidenced by the increase in metal concentrations was quite large. The positive correlations between the concentrations of Mn and Fe and other heavy metals in waters of the studied ponds indicate that they were subjected to redox driven remobilization processes. The obtained relationships suggest that sorption and dissolution of Fe compounds played an important role in the migration of Zn in SP and MP, Cd and Pb in MP, while circulation of Mn compounds could affect the migration of Pb in SP, Cd, Pb and Zn in MP, what was also observed in other water bodies [15, 19].

The obtained results indicated that organic matter (expressed as BOD_5 and LOI) play an important role in the migration of heavy metals in the studied ponds. It is known that functional groups of humic substances which are a mixture of fulvic and humic acids bind heavy metals (Cd, Pb, and Zn), and in this way modify metal bioavailability, their transport and content in water environment [21]. In reservoirs characterized by a high content of dissolved organic matter (DOM), the proportion of metals (Cd, Pb, and Zn) bound in complexes with DOM can reach 60–98%. In the Matylda catchment, large portion of metals probably entered ponds in the form of metal-humic complexes leached from the swampy soils of the valley bottom, the forested catchment or from the bed of numerous ditches covered with the fallen and decaying leaves. It is known that leaching of recent photosynthate (leaf litter, root exudates, decaying fine roots) or microbiological decomposition processes of organic matter are the most important source of DOC [22]. Decomposition processes promote acidification of soil substrate, increase the content of humic substances, reduce forms of mineral substances (such as metals, ammonia) and decrease of pH in draining water. Appearance of high or maximum content of heavy metals, organic matter (expressed as LOI, BOD_5) and NH_4^+ accompanied by low pH in the water of the studied ponds, especially in the near-bank shallows in winter and periodically in summer may indicate these phenomena.

The fluctuations of the contents of dissolved metals in pond waters were probably influenced by seasonal pattern of plant growth and decay. Thus lower metal concentrations during vegetation period might also be related to some extent to metal uptake by macrophytes and algae, which developed in the studied ponds during the growing season [10]. Many annual macrophytes release significant quantities of C, N and P and metals [23] to the surrounding water after decay. Macrophytes, especially submerged species, growing in the studied ponds contained increased metal (mainly Pb and Zn) concentrations [4] therefore their senescence and decay may be an important source of metals. Additionally, decomposition of the organic matter affects decrease of pH which favors release of metals from the sediments. The obtained results indicate that water pH control to the large extent (negative correlations) concentrations of all heavy metals in the ponds situated on the Matylda Stream what was also proved in many other water

bodies [17, 18]. Therefore the highest metal concentrations (especially Cd and Zn) were usually observed in all ponds in winter months when pH was the lowest.

The considerable fluctuations in metal concentrations in the studied ponds controlled adaptation of planktonic communities to persistent heavy metal contamination [10]. In the cascade of ponds (SP-MP-LP), the species resistant to high concentration of heavy metals and characteristic for waters contaminated with heavy metals like *Achnantes cryptocephala*, *A. minutissima*, *Surirella ovata* and *Eunotia exigua* were noted [10]. Both diatoms and green algae present in the investigated fishponds were described as species tolerant to heavy metals and high pollution. High concentrations of Zn and Pb in dissolved form in the water of SP were reflected in their high contents in shoots of *Myriophyllum spicatum* [4]. The process of biosorption of some metals on the surface of *M. spicatum* may be very fast (about 20 min) and followed by their slow accumulation and translocation to the biomass [24]. *Myriophyllum* shows much higher capacity to absorb heavy metals and lower tolerance against stress conditions than *Ceratophyllum* [25]. Decline of *Myriophyllum* and continuous presence of *Ceratophyllum* in SP in the whole vegetation season were probably caused by water pollution by the metals [4]. Therefore periodical appearance of high metal concentrations in the studied ponds may have a detrimental effect on biota.

The obtained results showed that the occurrence of high concentrations of heavy metals in the Matylda ponds were affected by the distribution of contaminated sediments both within ponds and in the valley bottom and by periodically varied physical and geochemical processes. Pond waters were more perceptible in near-bank parts than in the central ones (significant differences in the concentrations of Mn in SP; Mn, Fe, Zn, and nitrates in LoP; higher median concentrations of Cd (2.4 times) and Mn (1.6 times), and maximum concentrations of Pb, Mn and Fe). During most of the year the concentrations of heavy metals in dissolved forms (except for Zn) were similar to those found in slightly polluted rivers [26]. Higher than average concentrations of heavy metals reaching up to 8.5 µg Cd·dm^{-3}, 147 µg Pb·dm^{-3}, 800.3 µg Zn·dm^{-3}, 987.1 µg Mn·dm^{-3}, and 2532.8 µg Fe·dm^{-3}occurred only on some sampling occasions and were similar to those found in the Biała Przemsza River in this region, contaminated by active lead and zinc mines [27] and to other rivers in the industrial regions [28]. The decrease in the maximum concentrations of metals in pond waters (from UP to LP) might be associated with differences in the contamination of pond sediments [2] and soils in the catchment.

5. CONCLUSIONS

During this study heavy metal (Cd, Pb, Zn, Mn and Fe) concentrations in waters of five fishponds (UP, SP, MP, LP, and LoP) located in the Matylda catchment in the Upper Silesian Industrial Region in southern Poland were analyzed. All ponds for over

100 years utilized mine waters from the lead and zinc mine Matylda. The chemical composition of the pond waters (decreased amounts of sulfates and hydrocarbonates in comparison to surface water of rivers in southern Poland) reflected the geochemical background of the catchment, e.g. Triasssic dolomites bearing sulfidic Zn–Pb ore deposits and Holocene fluvial sandy sediments filling most of the valley bottom. The pond waters were usually well oxygenated and decrease in dissolved oxygen content (<2 mg $O_2 \cdot dm^{-3}$) due to organic matter decomposition was only periodically observed.

During prevailing part of the year, pond waters were characterized by low concentrations of most heavy metals in dissolved forms which were similar or slightly decreased if compared to those in moderately industrialized areas. Higher or maximum metal concentrations noted usually in winter and occasionally in summer and autumn could be related to annual cycling of organic matter production and degradation within each pond. The largest dissolved metal maxima including Fe and Mn occurred in ponds with the most contaminated sediments. Lower metal concentrations during vegetation period might be caused by metal uptake by algae and rise of pH during algae development.

High or maximum concentrations of heavy metals were induced mainly by "internal loading", e.g. remobilization of metals from contaminated, mostly organic bottom sediments [4], whereas external sources due to small amount and contamination of water supplied from the Matylda Stream seem to be less important [2]. Organic matter decomposition in winter resulted in an increase in the reductive conditions enhanced by ice cover and in the decrease of pH to about neutral promoting dissolution of Mn and Fe compounds, which may bound over 50% of heavy metal contents in bottom sediments. The highest metal concentrations at the end of summer and in early autumn (August –November) may be additionally explained by dying and degradation of algae and submerged macrophytes, enhanced at the end of the vegetation season. Influence of variable redox conditions on geochemistry of Mn and Fe compounds is confirmed by the negative correlation of oxygen content with Mn and Fe in some ponds (SP, LP, LoP and LP), whereas negative correlation of pH with heavy metal concentrations suggest influence of this parameter on content of Cd and Zn in all ponds and content of Pb in MP, Mn in MP and LP and Fe in SP and MP.

The organic matter originates also from fall and decay of leaves in the forested catchment dissected by numerous ditches draining contaminated sandy deposits of valley bottom and swampy areas in the middle reach of the Matylda Stream. The process was more intensive during winter when frozen subsurface favored washing during melting and rainy periods, which alternated with weak frost and snowing as well after longer raining periods of summer. Metals could be washed out and transported in the form of metal-humus complexes. This phenomenon is indicated by co-occurrence of maximum or high contents of heavy metals, organic matter (expressed as BOD5 and LOI) and N-NH$_4$ and slightly acidic or neutral pH in the pond waters, especially in the near-bank parts in winter and summer months.

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